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Using agricultural wastes to treat lead-contaminated water in Western Australia

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Using agricultural wastes to treat lead-contaminated water in Western Australia

This thesis is presented in fulfilment of degree if

Master of Engineering Science

Hanie Hashtroudi

Edith Cowan University

School of Engineering

2018

Declaration of originality

I hereby declare that all the information presented in this study has been obtained in accordance with ethical and academic principles. I also certify that I have fully referenced all materials previously published or written by another author in whole or in part, to the best of my knowledge, as defined by the Edith Cowan University's policy on plagiarism.

Hanie HASHTROUDI

Acknowledgements

Abstract

Aqueous solutions are becoming increasingly contaminated in all parts of the world (2015). Heavy metals are toxic contaminants that are mainly distributed in urban stormwater run-off and industrial wastewaters as a result of some mining operations, electronic assembly planting, battery manufacturing, and etching operations (Kadirvelu et al., 2001). Pb (II) is a heavy metal that causes significant damage in the human body. Drinking lead-contaminated water even at low concentrations may cause life-threatening conditions such as cancer, kidney damage, brain damage, and liver problems (El-Said, 2010). Therefore, it is necessary to remove lead from aqueous solutions.

Several conventional physical, chemical, and biological systems have been used to eliminate Pb (II) ions from contaminated aqueous solutions, including membrane filtration (Song et al., 2011), electrolysis (Deng et al., 2010), chemical precipitation (Cort, 2005), magnetic base methods (Ma et al., 2017), water filtration (Gohari et al., 2013; Magni et al., 2015), and adsorption techniques (Pehlivan et al., 2009). However, the cost of some of the cited techniques is prohibitively high, while others cannot remove low Pb (II) ion concentrations efficiently (Babel and Kurniawan, 2003; Volesky and Holan, 1995). Although adsorption is a reasonable process for removing dissolved lead from contaminated water, the cost of using conventional media (e.g. activated carbon and resin) make it cost inhibitive for the treatment of large quantities of wastewater (Cutillas-Barreiro et al., 2016; Demirbas, 2008). It also takes a long time in some cases to achieve adsorption equilibrium (Czinkota et al., 2002).

In recent decades, interest in the use of cost-effective adsorbents to reduce the expense of water treatment processes has intensified. Attention has been focused on natural agricultural waste materials such as seeds (Gilbert et al., 2011), fruit peel (Mallampati et al., 2015), nut shells (Taşar et al., 2014) , crop residues (El-Said, 2010), and fruit shells (Zein et al., 2010) as low-cost and environmentally friendly adsorbents which are highly efficient and generally available in large quantities (Ibrahim et al., 2010).

Against this backdrop, many agricultural residues are being produced every day, and they need to be managed. Using agricultural wastes to treat contaminated water is a low-cost and effective approach that deal with waste management and water treatment at the same time. This project describes an economically viable and practical way to utilize crop residues as adsorbents to remove toxic Pb (II) ions from lead-contaminated water. These agricultural waste adsorbents have a number of advantages; they are cheap and biodegradable, they have a porous surface, and are able to eliminate Pb (II) ions from contaminated water quickly and effectively.

Therefore, in this research two Western Australian crop residues were used as adsorbents to eliminate lead ions from aqueous solutions. The study was carried out in four phases: the first phase involved the selection and preparation of different local Western Australian agricultural wastes. Lupin straw and

canola stalk were collected from local farms and studied for their efficiency as two low-cost natural adsorbents that can remove dissolved Pb^{2+} ions from synthetic wastewater.

In the second phase, experiments were carried out to understand the equilibria of Pb (II) adsorption onto adsorbents. The effect of various environmental conditions such as contact time, pH, initial adsorbent dosage and adsorbate concentration were investigated.

The presence of different functional groups, chemical compositions, and the surface characteristics of the adsorbents were analysed in the third phase using energy dispersive X-ray spectroscopy (EDS), Fourier transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM) devices.

In the final phase, the obtained experimental data were validated using different isotherm models developed by Langmuir, Freundlich, Harkins-Jura, Redlich- Peterson and Halsey to describe the adsorption process based on the homogeneity of the surfaces of the adsorbents. Pseudo-first-order, pseudo-second-order, intra-particle diffusion, Elovich, and fractional power kinetic models were utilized to investigate the dynamic mechanism of lead adsorption onto adsorbents over time.

List of publications

Based on the obtained results, two papers were published in Desalination and Water Treatment journal as follows:

1. Treatment of lead contaminated water using lupin straw: adsorption mechanism, isotherms and kinetics studies; Hashtroudi (2019); doi: 10.5004/dwt.2020.25141.

2. Pb (II) ions sequestration from aqueous solutions by canola stalk: isotherms and kinetics studies; Hashtroudi et al. (2018); doi: 10.5004/dwt.2018.22420.

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List of abbreviations

WA: Western Australia

MP-AES: Microwave Plasma Atomic Emission Spectroscopy

SEM: Scanning Electron Microscopy

EDX: Energy Dispersive X-ray Spectroscopy

FTIR: Fourier Transform Infrared Spectroscopy

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Hanie HASHTROUI

Chapter-1

1 Introduction

1.1 Background

The world's main water resources are being polluted by the undesirable organic and inorganic wastes released into the environment because of the advance of civilization and rapid industrialisation. The presence of toxic contaminants such as heavy metals can damage the ecosystem and the human body (Duruibe et al., 2007). Although some heavy metals are essential parts of the biochemical process in the human body, the required level of consumption is on a micro or macro scale (Organization and Chemicals, 2002). Drinking contaminated water can be harmful to human health even at low concentration levels, and water quality improvement is therefore one of the most significant environmental issues in the world.

Toxic heavy metal ions are mostly found in urban stormwater run-off and industrial wastewaters. They are produced as a result of activities such as mining and quarrying, electronic assembly planting, battery recycling planting, and etching operations (Kadirvelu et al., 2001). Industrial wastewaters are discharged directly or indirectly into the environment and the pollutants it contains are transferred to primary water resources through surface run-off. Lead is one of the most harmful heavy metals for human health and it can remain in the system for years. Pb (II) can be found in urban stormwater runoff because of its presence in gasoline. This causes contamination of the soil near streets and drainage ways. Pb (II) can also accumulate in aquatic sediments and find its way through aqueous solutions as a result. Prolonged exposure to Pb has been shown to cause various life-threatening conditions such as several forms of cancer, kidney damage, central nerve system damage, brain damage, dermatitis, dizziness, and liver problems (El-Said, 2010). Lead has a half-life of about 600-3000 days and most of the inhaled Pb is accumulated in the bones (Hu et al., 2007).

Several conventional physical, chemical, and biological techniques have been used to remove toxic lead ions from aqueous solutions, including membrane filtration (Gholami et al., 2014; Song et al., 2011), oxidation (Parsons, 2004; Zhang et al., 2014), ion exchange (Iqbal et al., 2009b; Naushad et al., 2015), reverse osmosis (Khedr, 2013; Theepharaksapan et al., 2011), electrolysis (Deng et al., 2010), chemical precipitation (Cort, 2005), water filtration (Gohari et al., 2013; Thong et al., 2014), gutter system and hydrodynamic separators (2013), magnetic base methods (Guo et al., 2014; Khiadani et al., 2013; Ma et al., 2017), and adsorption techniques (Cutillas-Barreiro et al., 2016; Karnitz et al., 2007; Pehlivan et al., 2009). Although these methods are commonly used for Pb (II) removal, in some cases the use of these techniques is virtually precluded due to costs being prohibitively high and issues with efficiency at low Pb (II) concentrations (Babel and Kurniawan, 2003; Volesky and Holan, 1995). Table 1 lists some advantages and disadvantages of different water treatment techniques.

Table 1. Advantages and disadvantages of different water treatment techniques

Water purification techniques	Advantages	Disadvantages	References
Membrane filtration	- Can completely remove certain pollutants, including micro pollutants that are hard to pinpoint - Produces little waste - Reusable - Low energy consumption	- Cannot remove all kinds of pollutants - High initial maintenance cost - Size exclusion may limit additional Need to get replaced maximum every 10 years at least - Hazardous cleaning solution waste	(Wagner, 2001)
Coagulation	- Simple process - Cost effective - Removes many kinds of pollutants - Uses low cost chemical materials	- Chemicals need to be added during the process - Trained and qualified operator is required for construction design and maintenance and to administer the chemicals - Produces toxic waste sludge that causes a serious disposal problem - Time consuming process	(Carlson et al., 2000) (Yan et al., 2008)
Oxidation	- Eliminates many organic pollutants - Can remove some heavy metals	- High operational cost - Produces organic and inorganic oxidation by-products	(Fiessinger et al., 1981)
Ion exchange	- Speedy result - Quick installation - Easy waste disposal	- Normally not effective for low pH - In general, not effective for high contaminant concentrations - Not effective for removing a mixture of metals - High initial maintenance cost and energy consumption	(Helfferich, 1962) (Clifford, 1999)
Reverse osmosis	- Can remove smells or colours - Eliminates toxic metals and minerals	- Generally, recovers about 5% of the water that passes through them: the rest goes down the drain as wastewater. - Bacteria grows in storage units of treated water unless frequently fumigated	(Greenlee et al., 2009)
Electrochemical	- Environmentally friendly - High energy efficiency - Versatile	- High initial maintenance cost and energy consumption - Mass transfer restrictions between the electrodes - Residual pollutants need to be cleaned from the cathode after several cycles	(Chen, 2004) (Sirés and Brillas, 2012)
Chemical precipitation	Removes heavy metals from contaminated water	Sludge produced by the process needs to be disposed	(Kurniawan et al., 2006)
Adsorption	- Low cost - Environmental friendly - Potential as one of the most efficient methods for heavy metals and organic pollutants - Simple process	Does not remove microbes and bacteria	(Faust and Aly, 2013)

As Table 1 shows, these techniques have many advantages and disadvantages. For instance, chemical precipitation is widely used to remove contaminants from wastewater but discharging the sludge

produced is one of the main disadvantages of this process: it may cause long-term damage to the environment, creating a need for further treatment procedures. Another treatment technique is coagulation, which is based on sedimentation. This sedimentation results in an aggregation of pollutants, which is itself creates a serious disposal issue.

Some other water purification techniques such as ion exchange, electro chemical treatment, and membrane filtration have high initial maintenance costs, high energy consumption, and a slow treatment rate. Adsorption is an economic and simple process that is a highly efficient way to remove contaminants from wastewater even at low concentrations. The major disadvantage of adsorption is that microbes and bacteria cannot be removed using this technique.

Although adsorption is a feasible process for removing dissolved Pb (II) from aqueous solutions, the cost of using conventional media (e.g. activated carbon and resin) make it cost inhibitive for the treatment of large quantities of contaminated water (Cutillas-Barreiro et al., 2016; Demirbas, 2008). It is also takes a long time in some cases to achieve adsorption equilibrium (Czinkota et al., 2002).

The use of economical adsorbents to reduce the cost of treatment has intensified in recent years. Attention has been focused on various natural agro-waste adsorbents such as fruit peel (Anwar et al., 2010; Mallampati et al., 2015), fruit shells (Zein et al., 2010), nut shells (Babarinde and Onyiaocha, 2016; Coelho et al., 2014), husks and straw (Pehlivan et al., 2009; Singha and Das, 2012), and seeds (Gilbert et al., 2011; Jayaram and Prasad, 2009) as low-cost adsorbents which are highly efficient and mostly available in large quantities (Babarinde and Onyiaocha, 2016; Ibrahim et al., 2010; Lalhruaitluanga et al., 2010).

The research reported in this thesis provides a methodology for eliminating Pb (II) ions from synthetic wastewater using local agricultural wastes of Western Australia. The work provides a comprehensive investigation of different aspects of the adsorption process during the experiment. The findings of this research will help both agricultural waste management and water purification.

1.2   Description of the proposed research

A review of the literature reveals that canola stalk has not been evaluated as an adsorbent for the removal of lead ions from aqueous solutions. To the best of the author's knowledge, the literature does not include any information about using lupin straw as an adsorbent to remove contaminants from water and more particularly no study has been reported concerning the use of lupin straw as an adsorbent to remove Pb (II) ions from aqueous solutions. This research therefore represents a novel contribution to the research area. The use of canola stalk and lupin straw has several advantages: both agricultural waste adsorbents are cheap and biodegradable, they have a porous surface, and they are able to eliminate Pb (II) ions from contaminated water quickly and effectively. The main advantage of using natural raw materials as adsorbents is that the usage of chemicals during the water treatment process is minimized. In contrast, chemical and thermal treatments are generally expensive and energy intensive processes

and the possibility of releasing unwanted by-products from chemically treated adsorbents into water may create a need for further remediation procedures.

The present study tested the efficiency of lupin straw and canola stalk for the removal of lead in low concentrations from synthetic wastewater. The effects of experimental factors such as initial pH, contact time, adsorbent dosage, and adsorbate concentration were investigated. The obtained experimental data were then validated using different isotherm and kinetic models to investigate the adsorption process of Pb (II) ions onto the surface of the adsorbents. This research demonstrated that lupin straw and canola stalk are highly effective as economical, biodegradable and environmentally clean adsorbents for the removal of Pb (II) from contaminated water.

1.3   Aims and objectives

The aim of this research was to remove toxic Pb (II) ions from synthetic wastewater using local Western Australia agricultural waste products.

The following classification provides a brief review on the research objectives. The objectives of this research were to:

1. investigate the influence of experimental conditions such as pH, contact time, Pb (II) concentration, and adsorbent dosage on the adsorption capacity of Pb (II) onto selected agricultural waste adsorbents;
2. identify the influence of the surface characteristics of the adsorbents on the adsorption process of Pb (II) ions removal from synthetic wastewater;
3. quantify the maximum adsorption capacity and the amount of Pb (II) ions removed by the two adsorbents under different experimental conditions;
4. validate experimental data with different isotherm models and find the equilibrium time for each adsorbent;
5. find the most appropriate isotherm model to describe the adsorption process as a multilayer or monolayer adsorption based on the homogeneity of the adsorbents surfaces;
6. Investigate the dynamic mechanism of Pb (II) ion adsorption over time using different kinetic models and finding the best-fit kinetic model based on the correlation of coefficient values;

These objectives were met by answering the research questions introduced in Section 1.4.

1.4   Research questions

The following research questions were designed to enable the objectives of the research to be met:

1.   What is the effect of different experimental conditions on the adsorption capacity and the percentage of Pb (II) ions removed using selected agricultural waste adsorbents?
   1.1.   What is the effect of initial pH values on the adsorption capacity of Pb (II) ions removed using selected agricultural waste adsorbents?

1.2. What is the effect of different contact times on the adsorption capacity of Pb (II) ions removed using selected agricultural waste adsorbents?

1.3. What is the effect of initial lead concentrations and adsorbent dosages on the adsorption capacity of selected agricultural waste adsorbents?

2. What is the effect of the surface characterization of agricultural waste adsorbents on the adsorption process before and after experimental procedure?

3. How effective are selected adsorbents at removing Pb (II) from aqueous solutions?

4. What is the equilibrium time for each adsorbent to remove Pb (II) ions from contaminated water?

5. Which isotherm model best describes the adsorption of Pb (II) ions onto adsorbents?

6. Which kinetic model best describes the dynamic mechanism of the Pb (II) adoption process?

The present research aimed to study the feasibility of the removing Pb (II) ions from aqueous solutions using selected agro-waste adsorbents. As a result, it was essential to analyse the residual concentration of the pollutants and the adsorption capacity of the adsorbents. Adsorption capacity is one of the most important elements in the adsorption process. This is affected by various experimental conditions such as contact time, pH, initial adsorbate concentration, and initial adsorbent dosage. After all data relating to the analysis the surface morphology was collected, the maximum adsorption capacity and percentage of the Pb (II) removal were calculated. These values demonstrated the performance and reliability of the adsorbents for the sequestration of lead ions from aqueous solutions.

1.5 Processes involved in the research

The processes involved in this research are as follows:

1. Analysing the lead concentrations before and after each adsorption treatment to investigate the water quality.

2. Monitoring changes in the residual lead concentrations with the change of experimental parameters.

3. Analysing the surface characteristics of the adsorbents before and after each experiment.

4. Finding the equilibrium time for each adsorbent.

5. Finding the adsorption capacity and percentage of lead adsorbed onto adsorbents surfaces.

6. Comparing different isotherm parameters and finding the best isotherm model to describe and investigate the adsorption process.

7. Comparing different kinetic parameters and finding the best kinetic model to describe the dynamic behaviour of the adsorption process.

8. Comparing the results obtained from the study of different selected adsorbents to evaluate the efficiency and performance of the adsorbents in the elimination of Pb(II) from aqueous solutions.

1.6   Significance of this project

Water resources around the world are becoming increasingly toxic and contaminated. At the same time, many agricultural processes are producing increasing amounts of waste material, and these materials need to be managed effectively. Using these agricultural waste materials to treat contaminated water is a low cost and effective way to deal with the two areas (water treatment and waste management) at the same time. Using chemically treated adsorbents may create a need for further remediation procedures to clean the water post-treatment, but using raw materials reduces the possibility of releasing unwanted by-products into the water. This project identified a feasible way to utilize agro-wastes as adsorbents to remove toxic Pb (II) from lead-contaminated water. The study tested the efficiency of lupin straw and canola stalk for the removal of lead in low concentrations from synthetic wastewater.

1.7   Thesis outline

Chapter 1: Introduction

This chapter presented the overall summary of the proposed research, including the aims and objectives of the work, the research questions, the processes involved in the research, and the significance of the project. The remainder of the thesis is structured as follows:

Chapter 2: Literature review

This chapter reviews the research that has been carried out previously and highlights the gaps that the present work aimed to investigate. Investigating the gaps and issues with previous studies helped the researcher to develop deep understanding of the research area. The chapter is divided into four sections. Section 2.2 describes the adsorption process and explains how different adsorbents can remove contaminants from water. Section 2.3 explores the use of agricultural waste adsorbents as low-cost and environmental friendly materials. Section 2.4 focuses on the research literature about the removal of lead from aqueous solutions. Section 2.5 reviews the research relating to the use of lupin straw and canola stalk as adsorbents to remove contaminants from aqueous solutions.

Chapter 3: Methodology

This section describes the experimental set up and sampling procedures of the experiments. The instruments and chemicals used during the experimental work and material preparation are also discussed in this section. A process schematic is presented at the end of this section to show the whole experiment and facilitate understanding of the whole procedure.

Chapter 4: Theory of isotherm and kinetic models

This chapter explains the theory behind the different isotherm and kinetic models used and describes how all the parameters of isotherm and kinetic equations were calculated. This chapter also explains

how experimental data was evaluated using these equations to understand the adsorption process based on the theory and assumption behind used isotherm and kinetic models.

Chapter 5: Lupin straw - results and discussion

This chapter presents all the data from the different experimental conditions and the findings relating to the surface characteristics of lupin straw. All of the calculated parameters obtained from the experimental data are reported in this section, and the plots and results of the isotherm and kinetic models are indicated.

Chapter 6: Canola stalk - results and discussion

This chapter mirrors chapter 5 but presents all the data from the different experimental conditions and the findings relating to the surface characteristics of canola stalk. All of the calculated parameters obtained from the experimental data are reported and the plots and results of the used isotherm and kinetic models are presented.

Chapter 7: Conclusions and recommendations for future work

The overall conclusions and recommendations for future work are presented in this chapter.

Chapter-2

2 Literature review

2.1 Introduction

There are increasing concerns, around the world, about the discharge of heavy metals from industrial activities into the environment. These contaminants are not degradable so linger in the soil and environment for a long time. Consuming these undesired elements can cause different levels of toxicity in humans and animals. Mohammadpour et al. (2016) stated that eating the agricultural products grown in contaminated soil increases the health risks in line with the level of heavy metals adsorbed into agricultural products bodies. It is also stated that the waste products are usually dumped in the soil and then the contaminants make their way into the food chain. Recent studies have shown that lead is a highly toxic element and consuming it, even at low concentrations, causes life-threatening diseases all around the world (Fadzil et al., 2016). This element is mainly released into the environment from industrial activities, paints, gasoline, and storage batteries. It then transfer to the human body through drinking water and food consumption (Prüss-Üstün et al., 2004). In recent decades, various agricultural waste adsorbents have been examined in regard to their capacity to remove toxic heavy metals from aqueous solutions. A number of studies have been carried out to evaluate the efficiency of using agricultural wastes as adsorbents, including: crop straw (Chen et al., 2011; Robinson et al., 2002; Tong et al., 2011), fruit shells (Hamza et al., 2016; Mallampati et al., 2015), seeds (Mushtaq et al., 2016; Okpareke et al., 2016), peels (Annadurai et al., 2003; Anwar et al., 2010), nut shells (Altun and Pehlivan, 2007), barks (Cutillas-Barreiro et al., 2014; Mohan et al., 2014; Paradelo et al., 2016), leaves (Fadzil et al., 2016), and roots (Mukaratirwa-Muchanyereyi et al., 2015).

A review of the literatures relating to agricultural waste adsorbents under different experimental conditions has been carried out and presented in Appendix II. Appendix II is a tabulation of the significant points raised in the literature in regard to the use of specific agricultural waste adsorbents to treat wastewater. Most researchers have used a batch adsorption technique under different experimental conditions, adsorbent grain sizes, and target pollutants to establish different aspects of the adsorption process. The information presented in Appendix II enables us to compare the adsorption capacity of different agricultural waste adsorbents to study the reliability of these materials for the elimination of toxic contaminants from aqueous solutions under various experimental and operational conditions. Scrutiny of the literature on different agricultural waste adsorbents also provides a thorough overview, which supports the systematic research pathway developed in this work. More importantly, comparison of previously done studies renders valuable information about the knowledge gap and confirms the extra work required in this field of study.

The review of literature about agricultural waste adsorbents provides information about the effects of experimental conditions such as pH, contact time, metal concentration, and adsorbent dosage on the

adsorption process. This enables the present work to compare the efficiency of different bio-sorbents to eliminate heavy metals from polluted water and it can help in the identification of gaps and flaws in previous studies. Recent studies have highlighted the high yield of agricultural wastes as adsorbents in the removal of heavy metals from wastewater (Desta, 2013; Krishnani, 2016; Rajczykowski and Loska, 2016).

Several aspects of the elimination of heavy metals using bio-sorbents are discussed in this chapter. Attention is mostly focussed on the use of bio-sorbent crop residues (wheat, barley, canola, lupin, and oat) which are produced in large quantities in Western Australia. The primary focus of this literature review is to peruse previous research work on the adsorption of lead ions from aqueous solutions.

2.2   Adsorption process

Adsorption is simply the attachment of contaminants or substances from liquid or gas to the adsorbent based on the physical forces which is called "Physisorption" (Sing, 1985) or chemical bond "Chemisorption" (Ho and McKay, 1998). Adsorption process is mainly based on van der wales forces or chemical bond which depends on the nature of the adsorbent and contaminants. In physisorption, binding energy and intermolecular forces between adsorbates and adsorbents play important roles in the adsorption process. Another key parameter in physisorption is the pores on the surface of the adsorbent. The adsorbate usually goes through the surface into the pores of the adsorbent's particles during the process. Sometimes, the adsorbates just attach in the micro pores of adsorbents based on physical or chemical interactions. When we are considering the adsorbent surface, it is essential to differentiate between the outer surface and inner surface. Mostly the outer surface of the adsorbent particles is responsible for the mass transfer while the inner surface, which is equal to sum of the pores surfaces, is responsible for adsorbate uptake. The adsorption process is highly dependent on the pore structure and size of the adsorbent particles (Rouquerol et al., 2013).

On the other hand, mass transfer takes place on the outer surface of the adsorbent in four different transform stages as: convection, film diffusion, grain diffusion and attachment. The transportation of the adsorbate particles from the aqueous phase onto the boundary layer of the adsorbate is called convection. Before the adsorption equilibrium has been reached, the concentration of the pollutants in the aqueous phase is higher than the adsorbate surface. Therefore, this difference in concentration is the driving force that causes the adsorbate particles to move from the boundary layer into the surface of the adsorbent. This process is called film diffusion. The next stage is called grain diffusion which is transportation of adsorbate particles from the surface of the adsorbent into the pores of the adsorbent. The final stage is the attachment. At this stage, the adsorbate particles attach to the micro- pores of the adsorbent based on either chemical or physical interactions. Generally, film diffusion effects on kinetics and speed of the adsorption process. Figure 1 demonstrates four adsorbate transport stages in the adsorption process.
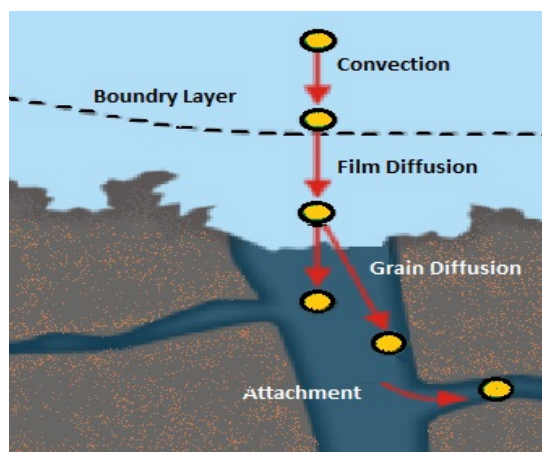
Figure 1. Adsorbate transport stages in the adsorption process

There are other important factors which have a significant effect on the kinetics of the adsorption process and should be considered during experimentation. First and foremost, the pore structure and size of the adsorbent particles affects the speed of the adsorption. Usually, the adsorption is quicker for the smaller particle sized adsorbents based on the diffusion paths. Similarly, pH and contact time have a remarkable effect on the adsorption kinetic and capacity of the adsorbents. Moreover, the concentration of the contaminants and the dosage of the adsorbates also have significant impacts on the adsorption process. The adsorption technique is designed for environmental purposes. Due to the physical and chemical interactions involved, it is mainly used in water treatment processes.

2.3 Agricultural waste adsorbent

Agricultural wastes are low-cost, biodegradable, and natural materials that have commonly been used for the removal of contaminants from aqueous solutions. A considerable amount of research has been published on using wheat straw as an adsorbent for water treatment application. A number of researchers have reported the different adsorption capacities of wheat straw under various experimental conditions.

Gorgievski et al. (2013) studied the removal of Cu, Zn, and Ni ions using wheat straw. Based on the experimental results, 76% of Cu, 90% of Zn, and 80% of Ni were eliminated from the water. The maximum adsorption capacities of wheat straw in regard to the removal of Cu (II), Ni (II), and Zn (II) were reported to be 5 mg/g/, 2.5 mg/g, and 3.25 mg/g respectively. The equilibrium time was 60 minutes. Although Gorgievski stated that the anionic hydroxyl functional groups on the wheat straw were mainly responsible for eliminating Cu (II) ions, there is a need for an investigation into the influence of the other anionic functional groups on the surface of the crop residues on the adsorption of cationic pollutants. Gorgievski also reported that the obtained experimental data were well modelled by the pseudo-second-order kinetic and Langmuir isotherm equations. The optimum pH to remove Cu ions was found to be 6.7. Similarly, Dang et al. (2009), stated that the optimum pH to remove Cu (II) was observed to be around 7.0. They published a study about adsorption of Cd and Cu using wheat straw

between pHs of 4.0 and 7.0. The authors achieved the removal of 87% of Cu and 80% of Cd after 3.5 h and 2.5 h equilibrium time, respectively. The authors stated that the maximum adsorption capacity of cadmium was found to be 3.5 times higher than the result presented by Miretzky et al. (2006). Although, wheat straw has a significant potential to be a low-cost adsorbent for the removal of Cu and Cd, questions have been raised about the efficiency of wheat straw for the removal of contaminants in low concentrations (less than 50 ppm) from aqueous solutions. Some agricultural wastes contain acidic sites such as phenolic and carboxylic and others may have oxygen-containing groups. The presence of different functional groups on the surface of different adsorbents affects the optimum pH values and needs to be explored. In addition, finding an agricultural waste adsorbent with a lower equilibrium time is also needed to reduce the cost of the process.

Kumar et al. (2000) used alkali-treated and xanthate-treated wheat straw to remove chromium from aqueous solutions. The authors stated that wheat straw contains 30% to 40% cellulose. They first treated the cellulose with alkaline and transformed $-CH_2OH$ groups into sodium alkoxide groups. Then the treatment was followed using carbon disulphide to change it to xanthate. The adsorption data presented for Cr removal demonstrated 77-87% removal efficiency for alkali-treated wheat straw as well as 82-99% for xanthate-treated straw. Both threated straws removed Cr effectively. However, the effect of the presence of xanthate groups as a unidentate ligand on the adsorption process needs more investigation.

Contrary to previous research, Özer et al. (2004) applied acid treatment to wheat bran. Sulfuric acid was utilized to modify wheat bran. The modified wheat bran was then used to remove Cu from contaminated water. The researchers studied the effects of initial pH, contact time, contaminant concentration, adsorbent dosage and temperature on the adsorption process. The result showed a significant increase in adsorption between pH=5 to 7 because of the participation of copper ions as insoluble $Cu (OH)_2$. More importantly, increasing the temperature significantly improved the adsorption of copper. The removal percentage of Cu was reported to be 96.4% which shows impressive efficiency of acid-treated wheat straw in Cu removal from water.

Özer and Özer (2004) published a paper in which the adsorption of Cr (VI) from polluted water using sulfuric acid-treated wheat straw was described. They analysed the effect of pH on the chromium adsorption process and claimed that by increasing the pH from 1.5 to 4 the adsorption of Cr decreased. Therefore, the optimum pH measured as 1.5 at which the percentage of Cr removal was 98%. This study reported the high adsorption capacity for Cr (VI) by sulfuric acid treated wheat straw (133.33 mg/g); however, comparison of this value with the adsorption capacity of other agro-waste adsorbents is difficult due to differences in experimental conditions.

A few years later, Han et al. (2010), applied citric acid-modified wheat straw to investigate the adsorption properties of copper ions. Based on the amount of carbonyl groups that were generated on

the surface of the modified wheat straw, the possibility of interaction between carboxyl groups as proton donors with positive metal ions was increased. Therefore, the authors concluded that modified wheat straw is more reliable adsorbent than untreated wheat straw regarding the removal of single metal ions. Unfortunately, there has not been enough research on the use of citric acid-modified wheat straw in the removal of heavy metals from water, and this research cannot therefore be relied on for the present work.

Factors found to be influencing the adsorption capacity of wheat straw have been studied by Chojnacka (2006). Chojnacka, in part of his research, investigated the maximum adsorption capacity of wheat straw for the removal of Cr (III) from water and examined the effect of experimental parameters including contaminant concentration, pH, and temperature (between 20 and 60°C) on the adsorption process. Although the intermediate adsorption capacity for wheat straw was reported, there has been little discussion about improving the adsorption process efficiency by increasing the adsorbent dosage. Adding alkaline or acid for treatment of wheat straw to increase the adsorption capacity may cause a need for further remediation procedure to remove undesired by-products. Apart from the difficulties of removing undesirable added chemicals, this procedure makes the cost of the adsorption process prohibitive.

Pehlivan et al. (2009) utilized barley straw to remove Cu and Pb from aqueous solutions. The optimum pH for the maximum percentage of pollutant removal was reported to be 6.4. The authors state that increasing the pH leads to decrease the amount of heavy metals adsorbed onto the barley straw surface. Although barley straw was able to remove 88% of Pb and 69% of Cu from aqueous solutions, there has been no study on the surface characteristics and morphological features of barley straw to identify the functional groups which are responsible for the adsorption process. Moreover, Pehlivan et al. (2009) did not investigated the isotherm and kinetic behaviour of the adsorption mechanism.

Maleki et al. (2011), also employed barley hull as a low-cost adsorbent to remove cadmium from raw water. The authors stated that barley hull removed 95.8% cadmium effectively at pH=9 after 180 minutes. Although, barley hull performed very well for the removal of cadmium from contaminated water, no information is provided about the chemical composition and surface characteristics of the barley hall. Therefore, debate continues about ways to improve the heavy metal attracting components to increase the adsorption capacity.

Oei et al. (2009), modified barley husk by cetylpyridinium chloride to eliminate acid blue 40 and reactive black 5 from contaminated water. The adsorption capacities of 1.02×10^{-4} mol/g and 2.54×10^{-5} mol/g were obtained for the removal of acid blue 40 and reactive black 5, respectively. The pseudo-first-order kinetic model and the Langmuir isotherm equation were used to describe the adsorption mechanism. The authors claimed that modified straws have positive charges on the surface which attracts negatively charged contaminants. What is not yet clear is the efficiency of using

cetylpyridinium chloride-modified barley husk as adsorbent for the removal of heavy metals from aqueous solutions. Likewise, no previous study has been found which adequately covers the effect of experimental conditions such as contact time, pH, adsorbent dosage and adsorbate concentration on the adsorption capacity of cetylpyridinium chloride modified barley husk when removing heavy metals from contaminated water.

Citric acid-modified barley husk was examined by Pehlivan et al. (2012) in regard to the removal of copper ions. This experiment reported the high equilibrium capacity of Cu for modified barley husk (31.71 mg/g) in comparison with untreated barley straw (4.64 mg/g). The results of this study indicated that acid-treated barley husk has great potential to be used as an adsorbent for water treatment applications. Although, the findings of Pehlivan et al. (2012) explain the efficiency of using citric acid treated barley residue for removal of copper, removal of other toxic heavy metals needs to be investigated.

Previously, Al-Asheh and Duvnjak (1999) conducted research into the sorption capacity of canola meal when removing heavy metals from contaminated water. Canola meal is a by-product of canola oil. Canola meal contains 38% proteins as a main component responsible for heavy metal uptake (Kuyucak and Volesky, 1989). The study showed that canola meal can be used for single heavy metal removal. The adsorption capacity of canola meal for the removal of five heavy metals was reported as: Zn> Cu> Cd> Ni> Pb. In addition, the optimum pH for metal adsorption was found to be 5.2. Al-Asheh and Duvnjak (1999) provided a considerable amount of information about how various parameters affected the process; nonetheless, there is currently very little comparison of the sorption of heavy metals based on their electronegativity either from a single metal solution or from a mixture of heavy metals.

So far little attention has been paid to oat straws as adsorbent. Gardea-Torresdey et al. (2000), studied the ability of oat hull to eliminate Cr (VI) and Cr (III) from wastewater under different time and temperature conditions. They observed about 90% bindings of Cr (III) was observed at pH=6, while 32% of the Cr (VI) was removed at pH= 2. Therefore, utilizing oat residue may have the advantage of eliminating Cr (III) from contaminated water.

Although extensive studies have been carried out on the adsorption process, identifying the components which are responsible for the adsorption process may enhance our understanding of certain limitations of the adsorption mechanism in the context of the elimination of toxic pollutants from aqueous solutions.

Most of the articles failed to consider whether the agricultural waste adsorbent residues (that showed high adsorption efficiencies) were readily available or available in the quantities required. Nor did they consider production costs for the different crops. Therefore, availability – in terms of both access and amount – may have a significant impact on the cost of the adsorption process in the industrial scale.

2.4   Lead removal from aqueous solutions using agricultural waste adsorbents

Due to the increased release of Pb (II) ions in the environment, Sahu et al. (2009) utilized activated rice husk to eliminate lead from wastewater. The rice husk was treated by sulfuric acid to become activated carbon. The authors performed the experiments in a modified multi-stage bubble column reactor. The maximum percentage of lead removal was measured 77.15%. During the experiments, the pH and temperature were kept constant at 7.15 and 25° C respectively. A column reactor was designed for this study; however, the effect of different experimental conditions on the efficiency of the designed system remains a matter of debate. In addition, no information is provided about the comparison of the efficiency of activated rice husk in the removal of lead ions in a batch study and a study using purpose-designed column reactor. Therefore, it cannot be concluded that activated rice husk behaves similarly under different experimental conditions in batch reactors. Negi et al. (2012) experimented on the removal of lead from synthetic and industrial waters using onion and garlic wastes. The pH of the solutions was varied from 2 to 7 and the optimum pH value was reported pH 5. Different temperatures in the range of 30- 60° C were examined and the ideal temperature was achieved at 50° C. The equilibrium time of 30 min was obtained when 5 g/L of adsorbents were added to 50 ppm of lead solutions. The Langmuir isotherm and pseudo-second-order kinetic models described the adsorption process well. Onion waste and garlic waste had maximum lead adsorption capacities of 9.95 and 10.49, respectively.

Yahaya and Akinlabi (2016) utilized HNO_3-treated Theobroma cocoa-pod husk to eliminate lead. Further modification was carried out using EDTA mixed with pyridine for 24 hours. The equilibrium time is reported to be 50 min and 94.6% of lead was removed successfully. The kinetic studies showed that the experimental data fitted into pseudo-second-order equation best with the correlation of coefficient value range of 0.98 to 1. According to the modification procedures and amount of chemicals used, the process does not seem to be cost effective. Different bio-sorbents (rice straw, rice bran, rice husk, coconut shell, neem leaves, and hyacinth root) were used in the elimination of Pb (II) ions from the effluent of the battery industry (Singha and Das, 2012). All the experiments were carried out at 30° C with a metal concentration range of 5-300 mg/L. The adsorbents were treated by NaOH and sulfuric acid first and sieved to under 350 μm size. The optimum pH values were found at 5. Experimental data fitted well in pseudo-second-order kinetic model and the Langmuir isotherm best described the adsorption process. After the remediation procedure, 92% of lead from the battery industry waste were removed by rice straw; 90% was removed by rice bran; 89% by rice husk; 96% by coconut shell; 95% by neem leaves; and 95% by hyacinth roots.

Ogunleye et al. (2014) examined phosphoric acid-modified banana stalk as adsorbent to remove lead from wastewater. The modification was followed by a dehydration procedure for 12 hours at 105° C and then carbonized in the absence of air for 2 hours at 800° C. The filtered carbonized adsorbent was mixed with 0.1 hydrochloric acid for 1 hour. After equilibrium time of 120 min the maximum adsorption

capacity was reported to be 200 mg/g. At the optimum pH of 8 about 97.9% was removed with a lead concentration of 250 mg/l. The experimental data fitted the Langmuir isotherm model with r^2 value of 0.99. The kinetic studies showed that pseudo-second-order model described the adsorption process best. While Anwar et al. (2010) were found the adsorption capacity of 2.18 mg/g for the elimination of Pb (II) using banana peel as adsorbent. The authors stated that the optimum pH was found to be 5 and about 85% of lead was removed. Comparing these two studies suggests that using plain banana peel to remove lead is not as efficient as using chemically and thermally treated peels to remove lead. In addition, chemical and thermal treatments are mostly expensive, time consuming, and energy intensive so are not cost effective when large quantities of agro-waste is involved.

Table 2 lists some of the previous studies on the adsorption of lead ions from aqueous solutions using different agricultural waste adsorbents.

Table 2. Adsorption of Pb (II) ions from aqueous solutions by different agricultural adsorbents.

Adsorbent	Particle size	Target pollutants	Optimum experimental conditions	Modification	Best fit isotherm model	Best fit kinetic model	Maximum adsorption capacity (mg/g) or (mmol/kg)	Removal percentage	References
Coconut husk	0.15-0.5 mm	Pb	pH: 5, Metal concentration: 30 ppm, contact time: 30 min, temperature: 100° C	-	Langmuir	Pseudo-second order	-	94	(Abdulrasaq and Basiru, 2010)
Soybean oil cake	-	Pb	pH: 6, Temperature: 15° C	K2CO3	Freundlich	Pseudo-second-order	244.9	-	(Erdem et al., 2013)
Date stem	0.3- 0.8 mm	Pb	pH: 2-4 Temperature: 30° C, contact time: 60 min	Nitrate solution	Langmuir Freundlich	Pseudo-second-order	5.15	97	(Yazid and Maachi, 2008)
Militia ferruginea plant leaves	125 μm	Pb	pH: 4, adsorbent dosage: 4g, contact time: 180 min	Sulfuric acid	Freundlich	Pseudo-first-order	3.3	97.3	(Mengistie et al., 2008)
Ailanthus excels tree bark	100-200 μm	Pb	pH: 4.5, contact time: 360 min	NaOH	Langmuir	Pseudo-second-order	22.72	-	(Waghmare and Chaudhari, 2013)
Cladophora rivularis hoek	-	Pb	pH:4	-	Freundlich	Pseudo-second-order	-	97	(Jafari and Senobari, 2012)
Flamboyant flower	-	Pb	pH: 5, Temperature: 32° C, contact time: 60 min	-	-	Pseudo-second-order	4.5	-	(Jimoh, 2012)
Gmelina arborea leaves	300 mesh	Pb	contact time: 90 min, adsorbent dosage: 5 mg/l	Citric acid	Freundlich	Pseudo-second-order	4.6	-	(Tijani et al., 2011)

2.5 Studies relating to the use of lupin straw and canola stalk as adsorbents

Hamzeh et al. (2011a) examined the use of canola stalk for the removal of acid orange 7 and Remazol black 5 from synthetic wastewater. The maximum adsorption capacity occurred at an optimum pH of 2.5 after 120 minutes. The experimental data fitted the Langmuir isotherm and pseudo-second-order kinetic models. Although a high percentage (>90%) of dyes were removed successfully, the potential of canola stalk to eliminate lead ions needs to be investigated. Amouei et al. (2014) presented a study on canola residues for the removal cadmium from aqueous solutions. The adsorption process fitted into the Freundlich isotherm equation and pseudo-second-kinetic model. This study revealed that the H^+ ions adsorbed much faster than cadmium due to the size of the H^+ ion which is smaller than the Cd ion. Therefore, the adsorption capacity of cadmium decreased at lower pHs. Likewise, at higher pHs the adsorption capacity of the cadmium decreased because of the increase in the number of hydroxyl ions on the adsorbent surface. At pH>7, sedimentation of cadmium ions was reported. Consequently, the optimum pH was found to be 6. Maleki et al. (2011) note that there is contradictory evidence regarding the optimum pH for cadmium removal, and this issue therefore quires further scrutiny and experimental examination.

Balarak (2014) utilized canola stalk as adsorbent to adsorb Cr (VI) from contaminated water. More than 99% of hexavalent chromium was removed at pH=3 after 75 minutes. The optimum adsorbent dosage and metal concentration were found to be 5 g/L ad 10 mg/L respectively. The adsorption capacity of the canola stalk was calculated to be 10.67 mg/g using the Langmuir isotherm. The adsorption mechanism was described with the pseudo-second-order kinetic model. The result showed that the adsorption process was significantly affected by the adsorbent dosage, as the percentage removal of Cr (VI) changed from 38% to 96% by increasing the canola stalk dosage from 1 to 5 g/L. This finding is similar to the results obtained by Kumar and Bandyopadhyay (2006b) for the removal of cadmium ions using rice husk.

A review of the literature reveals that canola stalk has not been examined as an adsorbent for the elimination of lead ions from contaminated water. This agricultural waste adsorbent has a number of advantages: it is cheap and biodegradable, it has a porous surface, and it is able to sequestrate Pb (II) ions from contaminated water quickly and effectively. Enayati et al. (2009) investigated the chemical composition and morphological properties of canola stalk. Their results indicated that canola stalk contains 17.3 wt% of lignin, 73.6 wt% of holocelluloses, 8.2 wt% of ash content, and 42 wt% of alphacellolose which is comparable with hardwoods and non-wood raw fibres. Due to the high percentage of lignin and cellulose, canola stalk raw fibres have a potential to be used as an adsorbent. The main advantage of using natural raw material as an adsorbent is that the usage of chemicals during the water treatment process is minimized. In contrast, chemical and thermal treatments of bio-sorbents are generally expensive and energy-intensive processes and the possibility of releasing (into the water)

unwanted by-products from chemically treated adsorbents may create a need for further remediation procedures.

Canola stalk has been used in a small number of studies to remove dye and hexavalent chromium from contaminated water (Balarak, 2014; Balarak et al., 2015; Hamzeh et al., 2011a; Hamzeh et al., 2011b). Therefore, the present study tested the efficiency of canola stalk for the adsorption of lead in low concentrations from synthetic lead-contaminated water. The influence of different experimental factors such as pH, contact time, canola stalk dosage, and lead concentration were studied. Based on the experimental data, the isotherm and kinetic modellings of the adsorption process were then investigated for the sorption of Pb (II) ions onto canola stalk.

To the best of the author's knowledge, the literature does not include any information about using lupin straw as an adsorbent to remove contaminants from aqueous solutions and more particularly no study has been reported concerning the use of lupin straw as an adsorbent for the removal of Pb (II) ions from aqueous solutions. This study therefore represents a novel contribution to the research area.

2.6   Conclusion

Ion exchange plays the most prominent role in the process of metal bio-sorption (Kratochvil and Volesky, 1998). Bio-sorbents vary in how effectively they sequestrate heavy metal ions because the adsorption process is under the influence of different experimental conditions. For instance, the pH of the solution has a significant influence on the adsorption capacity of the adsorbent and has a relation with the contribution of the functional groups in the adsorption process (Faust and Aly, 2013). It is also linked to the surface charge of the adsorbents. Although pH has a notable impact on the adsorption process, the variation of the pH solutions was not investigated in some of the journal articles. The initial metal concentration and adsorbent dosage also have an undeniable influence on metal sequestration. Increasing the adsorption capacity by increasing the initial metal concentration could be the consequence of the increased collisions between the adsorbate and the adsorbent surface (Wang et al., 2010). According to the literature, contact time is another experimental condition that needs to be considered in the adsorption process. Normally, the adsorption rate is rapid at the beginning of the experiment and gets slower until the equilibrium time is reached. When the adsorption reaches the equilibrium time, it means that the active sites on the surface of the adsorbent are saturated. This process is faster in some adsorbents than others. The size of the adsorbent particles and the temperature of the solution also affect the metal uptake efficiency. Particle size has a reverse relationship with the available surface area of the adsorbent. Decreasing the particle size could result in an increase in the available surface area of the adsorbent. Consequently, the possibility of intra-particle diffusion would increase. Some research papers stated that increasing the temperature led to a reduction in the metal sorption capacity of the adsorbent (El-Sayed et al., 2011). They reported that by increasing the temperature from 25° C to 55° C, the adsorption of Mn, Zn, and Cd was reduced from 39% to 13%, 52% to 38% and 34%

to 16% respectively. García-Rosales and Colín-Cruz (2010) stated that adsorption of lead increased by increasing the temperature from 20° C to 40° C. However, Park et al. (2010) reported that some physical deformations in the structure of the adsorbent have been observed by increasing the temperature. In this regard, most of the researchers have performed their experiments at ambient temperature. Although a variety of studies are conducted in adsorption area, several issues and limitations need to be investigated.

All in all, our understanding of the physical and chemical interactions between metal ions and the surface of the bio-sorbent under different operational and experimental conditions enables us to tackle the challenging issues behind the adsorption process. Development in identifying of active functional groups which are responsible for the adsorption process is also required. This work is important because it will facilitate the selection of appropriate agricultural waste adsorbents which will provide efficient adsorption interaction between the contaminant and the surface of the selected material. A lot of modification procedures have been used on the adsorbents to facilitate the ion exchange and metal uptake process, but the cost of the modifications needs to be considered as an important issue. The cost implication is an indispensable factor in relation to the commercialization of an economical water treatment process on an industrial scale. The present research hypothesises that utilizing highly efficient raw agricultural waste adsorbents will be a cost effective, feasible and natural way to eliminate contaminants from contaminated wastewater. This chapter has presented as survey of the literature relating to the removal of toxic heavy metals from contaminated water using agricultural waste adsorbents and Chapter 3 will outline the methodology adopted for the research described in this thesis.

Chapter-3

3 Methodology

3.1 Introduction

This chapter describes the experimental set up and sampling procedures of the experiments. The instruments and chemicals used during the experimental work and material preparation are also discussed in this chapter. A process schematic is also presented to show the whole experiment and facilitate understanding of the whole procedure.

For the purposes of this research, the main crop residues products of Western Australia were identified with help of the Department of Agriculture and Food of Western Australia and two of them were selected as adsorbents for the remainder of the work. All the agricultural waste materials used in this study were collected from Western Australia's local farms and used as inexpensive, natural, and safe adsorbents. After preparation of the adsorbents and the adsorbate solutions, the batch experiments were carried out in a variety of experimental conditions.

3.2 Adsorbent selection

Large areas of Western Australia are under cultivation, with many different crops and cereals. Appendix I provides a table relating to the quantity and dispersion of crop and cereal straws in Western Australia. The Department of Agriculture and Food, Western Australia (DAFWA) supports the growth of all crop industries in Western Australia from rain-fed winter cereals to irrigated horticultural crops.

Since 2007 some of the agricultural residues of Western Australia - such as wheat straw- have been converted to high quality gas or biochar through the pyrolysis process (heating with low oxygen levels) to become suitable fuel for gas engines or be used as soil nutrients.

Based on the information reported by the Department of Agriculture and food of Western Australia, an average of 13 million tonnes of grains such as wheat, barley, canola, pulses, lupins, oilseeds, and cereals are produced every year (DepartmentofAgricultureandFood, 2016). The bar charts (Figure 2 and Figure 3) demonstrate the straw yield crop average over five years and the average crop residue per shire in Western Australia. 40% of Australian's canola crop is grown in Western Australia.. Likewise, sweet lupin growing has doubled in WA since the late 1960s. Due to the wide range of agricultural residues that are produced every day in Western Australia, using them as adsorbents is a feasible, low cost, and effective way to both treat water and manage agricultural waste.

A number of studies have previously been done using wheat straw and barley straw for the elimination of contaminants from aqueous solutions. To the best of the author's knowledge, the literature does not include any information about using lupin straw as an adsorbent to remove contaminants from aqueous solutions and more particularly no study has been reported concerning the use of lupin straw as an adsorbent to remove Pb (II) ions from aqueous solutions. Similarly, a review of the literature reveals

that canola stalk has not been evaluated as an adsorbent for the removal of lead ions from aqueous solutions. Based on the presented information lupin straw and canola stalk, two of the main agricultural residues in Western Australia, were selected to be examined as adsorbents to remove Pb (II) from aqueous solutions in this study.
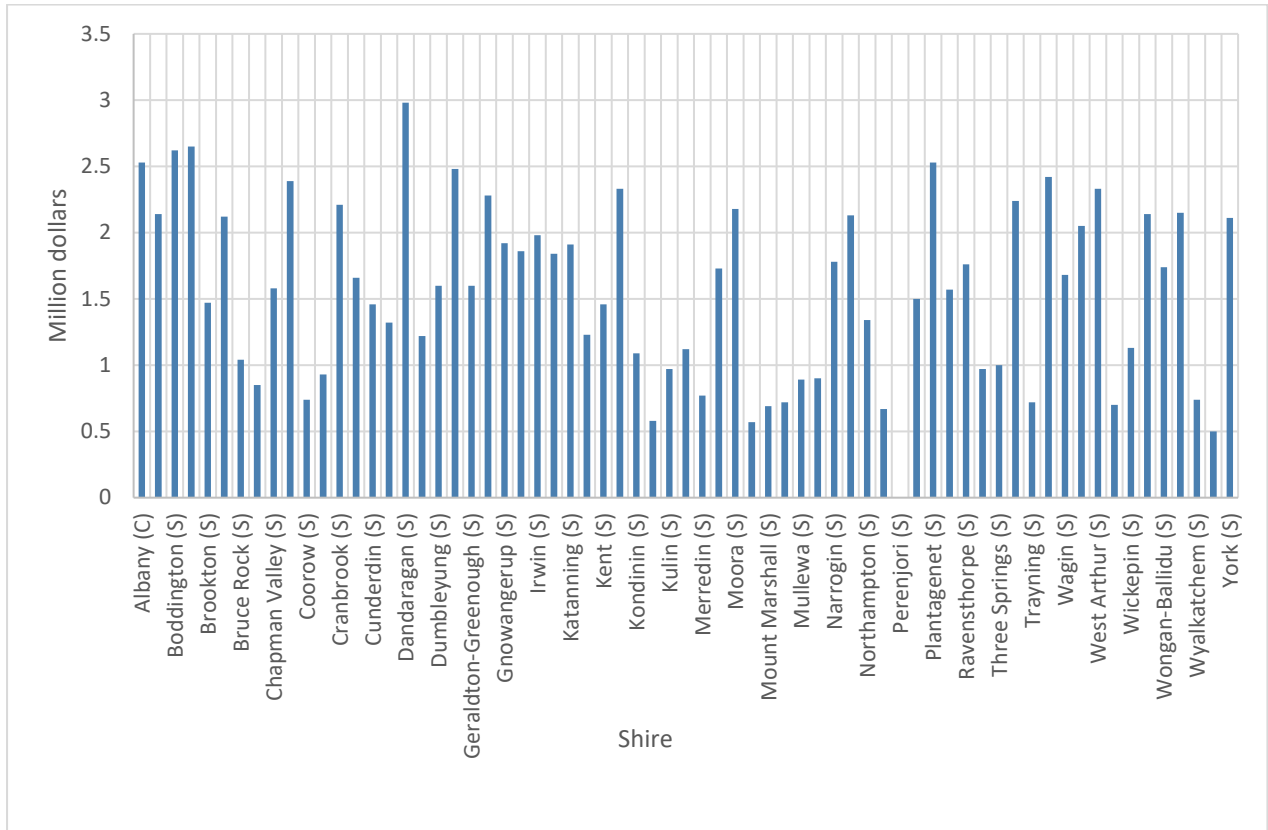
Figure 2. Straw yield /ha cereal crop average over five years
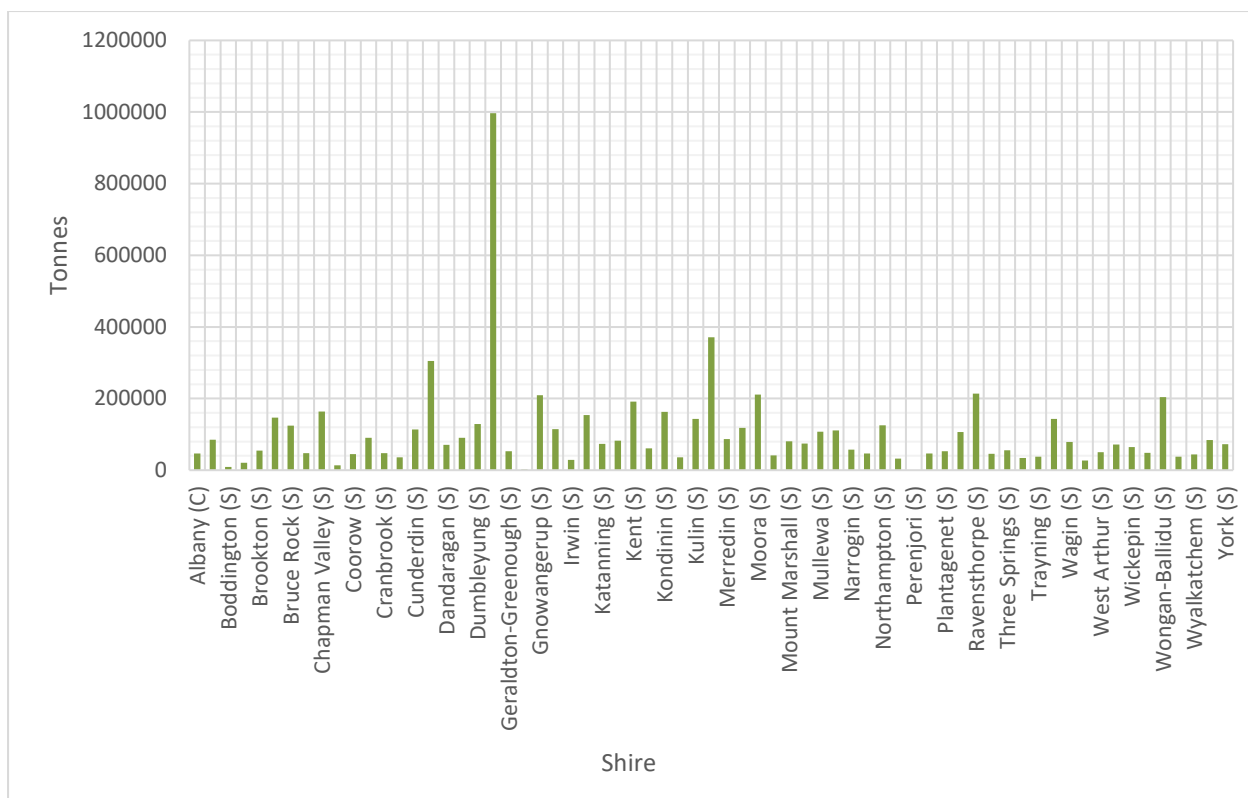
Figure 3. Average shire yield of crop residue (wheat, barley, canola, pulses, lupins, oilseeds, and cereals) (tonne)

3.3   Instruments and chemicals

In this study microwave plasma atomic emission spectroscopy (Agilent 4200 MP-AES) was used to analyse the concentration of lead ions during the experiments. Scanning electron microscopy (SEM, JEOL JSM-6000) was used to determine the roughness and characteristics of the surface of the adsorbents. The chemical composition of the lupin straw and canola stalk was investigated by energy dispersive X-ray spectroscopy (EDS, DX200s). Fourier transform infrared (FTIR, PerkinElmer UTAR Spectrum two) was used within a range of 4000-400 cm^{-1} to investigate functional groups on the surface of the adsorbents. The pH of the solutions was measured by a pH meter (Rowescience WP-90Z) and the sizes of the adsorbents were measured using a Mastersizer (Malvern 3000). Hydrochloric acid (0.1 mol/L) and sodium hydroxide (0.1 mol/L) solutions were used for pH adjustment during the experiment. All the chemicals used in this research were obtained from Agilent Technologies Australia and Merck Pty Ltd, Australia.

3.4   Adsorbate solution preparation

The adsorbate solutions were prepared through a serial dilution procedure using a high purity stock standard lead (1000 mg/L) solution. The required amount of stock solution was transferred to the volumetric flask containing deionized water and hydrochloric acid (HCL). The prepared adsorbate solution was diluted to the required different concentrations before starting the experiment.

3.5 Agro-waste adsorbent preparation

The lupin straw and canola stalk used in the present study were collected from local farms in Western Australia. Once collected, the agricultural waste materials were thoroughly washed with water several times to remove dust and dirt, followed by three thorough washes with deionized water to remove lighter soluble contaminants. The waste materials were then dried in an oven at 100° C for 24 hours. Thereafter, the dried adsorbents were ground and sieved to achieve the desired size of less than 300 μm.

3.6 Batch adsorption

In the present study the batch adsorption experiments were performed in 100 mL flasks. After adding the necessary amount of adsorbent, the prepared 100 mL solutions were shaken by a temperature-controlled mechanical shaker (RATEK OM11 digital orbital shaking incubator) at 200 rpm. The temperature was kept constant at 23°C during all the batch experiments. Different pHs, contact times, adsorbent dosages and adsorbate concentrations were tested during the experiment. The pH of the mixtures was adjusted by adding 0.1 M HCl and 0.1 M NaOH solutions. After stirring the samples for the predetermined desired contact time, the mixtures were filtered out and the aqueous phase of every sample was analysed for its Pb (II) concentration using MP-AES. Each experiment was replicated three times to reduce experimental errors. Different experimental parameters, such as initial adsorbent dosages (10-30 g/L), lead concentrations (5-15 mg/L), pHs (2-10), and contact times (5-120 min) were examined to determine the maximum adsorption capacity of the Pb (II) ions onto the surface of the lupin straw and canola stalk. The equilibrium contact times were determined for each adsorbent after testing different predetermined time intervals. The adsorption capacities of lead ions were calculated from the following equation:

$$q = \frac{(C_i - C_e)V}{D_i} \tag{1}$$

where, q is the adsorption capacity of the adsorbent (mg/g), C_i and C_e are the initial and equilibrium concentrations of adsorbate (mg/L), V is the volume of the contaminated solution (L), and D_i is the initial adsorbent dosage (g). The percentage of Pb (II) removal for each experiment was also calculated as follows:

$$\text{Lead removal}(\%) = \left[\frac{(C_i - C_e)}{C_i}\right] \times 100 \tag{2}$$

3.6.1 Sampling procedure

Table 3 demonstrates the procedure for the experimental data collection to investigate the effect of experimental conditions on the adsorption process of Pb (II) ions using lupin straw as adsorbent.

Table 3. Sampling experimental procedure to investigate the influence of different experimental parameters on the removal of Pb (II) ions using lupin straw.

Lupin straw	pH	Contact time (min)	Initial lead concentration (mg/L)	Initial adsorbent dosage (g/L)	Replication	Number of experiments
Effect of pH, set 1	2 4 6 7 8 10	120	5	10	3	18
Effect of pH, set 2	2 4 6 7 8 10	120	10	10	3	18
Effect of pH, set 3	2 4 6 7 8 10	120	15	10	3	18
Effect of contact time, set 1	Optimum	5 15 30 45 60 75 100 120	5	10	3	24
Effect of contact time, set 2	Optimum	5 15 30 45 60 75 100 120	10	10	3	24
Effect of contact time, set 3	Optimum	5 15 30 45 60 75 100 120	15	10	3	24
Effect of initial adsorbent dosage and adsorbate concentration, set 1	Optimum	Optimum	5	10 30 50	3	9
	Optimum	Optimum	10	10	3	9

Canola stalk	pH	Contact time (min)	Initial lead concentration (mg/L)	Initial adsorbent dosage (g/L)	Replication	Number of experiments
Effect of initial adsorbent dosage and adsorbate concentration, set 2				30		
				50		
Effect of initial adsorbent dosage and adsorbate concentration, set 3	Optimum	Optimum	15	10	3	9
				30		
				50		
Total						153

Table 4 shows the designed sampling procedure of lead removal onto canola stalk.

Table 4. Sampling experimental procedure to investigate the influence of different experimental parameters on the Pb (II) ions removal onto canola stalk.

Canola stalk	pH	Contact time (min)	Initial lead concentration (mg/L)	Initial adsorbent dosage (g/L)	Replication	Number of experiments
Effect of pH, set 1	2 4 6 7 8 10	120	5	10	3	18
Effect of pH, set 2	2 4 6 7 8 10	120	10	10	3	18
Effect of pH, set 3	2 4 6 7 8 10	120	15	10	3	18
Effect of contact time, set 1	Optimum	5 10 15 20 30 45 60 120	5	10	3	24
Effect of contact time, set 2	Optimum	5 10 15 20 30 45 60 120	10	10	3	24
	Optimum	5 10	15	10	3	24

Effect of contact time, set 3		15				
		20				
		30				
		45				
		60				
		120				
Effect of initial adsorbent dosage and adsorbate concentration, set 1	Optimum	Optimum	5	10	3	9
				30		
				50		
Effect of initial adsorbent dosage and adsorbate concentration, set 2	Optimum	Optimum	10	10	3	9
				30		
				50		
Effect of initial adsorbent dosage and adsorbate concentration, set 3	Optimum	Optimum	15	10	3	9
				30		
				50		
Total						153

In total, 306 experiments were performed to analyse the influence of the initial pHs, contact times, initial adsorbents dosages, and initial lead concentrations on the performance of the agricultural waste adsorbents used to sequestrate lead from aqueous solutions.

3.7 Procedure for finding optimum experimental conditions

3.7.1 Initial pH

The effects of pH on lead extraction were investigated by adding 1 g of adsorbent in 100 mL prepared lead solutions for each experiment. The lead concentrations were varied (5, 10 and 15 (mg/L)), and all the batch tests were carried out at 23° C. The pH of the mixtures was adjusted from 2 to 10 by adding 0.1 M HCl and 0.1 M NaOH solutions. The initial adsorbent dosage (10 g/L), contact time (120 min), and agitation speed (200 rpm) were kept constant at this stage. This procedure was performed for lupin straw and canola stalk separately. Each test was repeated three times and the residue of Pb (II) ions was then analysed using an MP-AES device. After obtaining the experimental data and calculating the adsorption capacity and percentage of lead removal, the optimum pH values for each adsorbent were found.

3.7.2 Contact time

The effects of different initial metal concentrations and contact times were studied at this stage. All the batch tests were performed in 100 ml flasks with different initial metal concentrations of 5, 10, 15 (mg/L) at optimum pH values. For each experimental test, 1 g of adsorbent was added to the lead

solution at 23° C. The contact time was ranged from 5 to 120 minutes for different lead concentrations to find the equilibrium time for lupin straw and canola stalk. The pH of the solutions (optimum pH), initial adsorbent dosage (10 g/L), and agitation speed (200 rpm) were kept constant during the experiments. This procedure was carried out for lupin straw and canola stalk separately and replicated three times. After analysing the lead concentrations after the experiments, the saturation equilibrium times of lupin straw and canola stalk while removing dissolved Pb (II) ions were determined. The obtained experimental data were also used for isotherm studies.

3.7.3 Adsorbent dosage and adsorbate concentrations

At this stage, the pH of the solutions (optimum pHs), contact time (equilibrium times), and agitation speed (200 rpm) were kept constant during the experiments. Initial adsorbent dosage was changed from 10 to 30 g/L adding to 100 mL lead solutions of 5, 10, and 15 mg/L at optimum pH values. This procedure was repeated for lupin straw and canola stalk separately, and each experiment was replicated three times. The effects of different initial adsorbent dosages on the percentage of lead ions removed were investigated. The obtained experimental data were used for kinetics studies as well.

3.7.4 Sampling process schematic

The experimental sampling process schematic for each adsorbent is outlined in as a flowchart and presented in Figure 4. The same sampling procedure was used for both lupin straw and canola stalk.
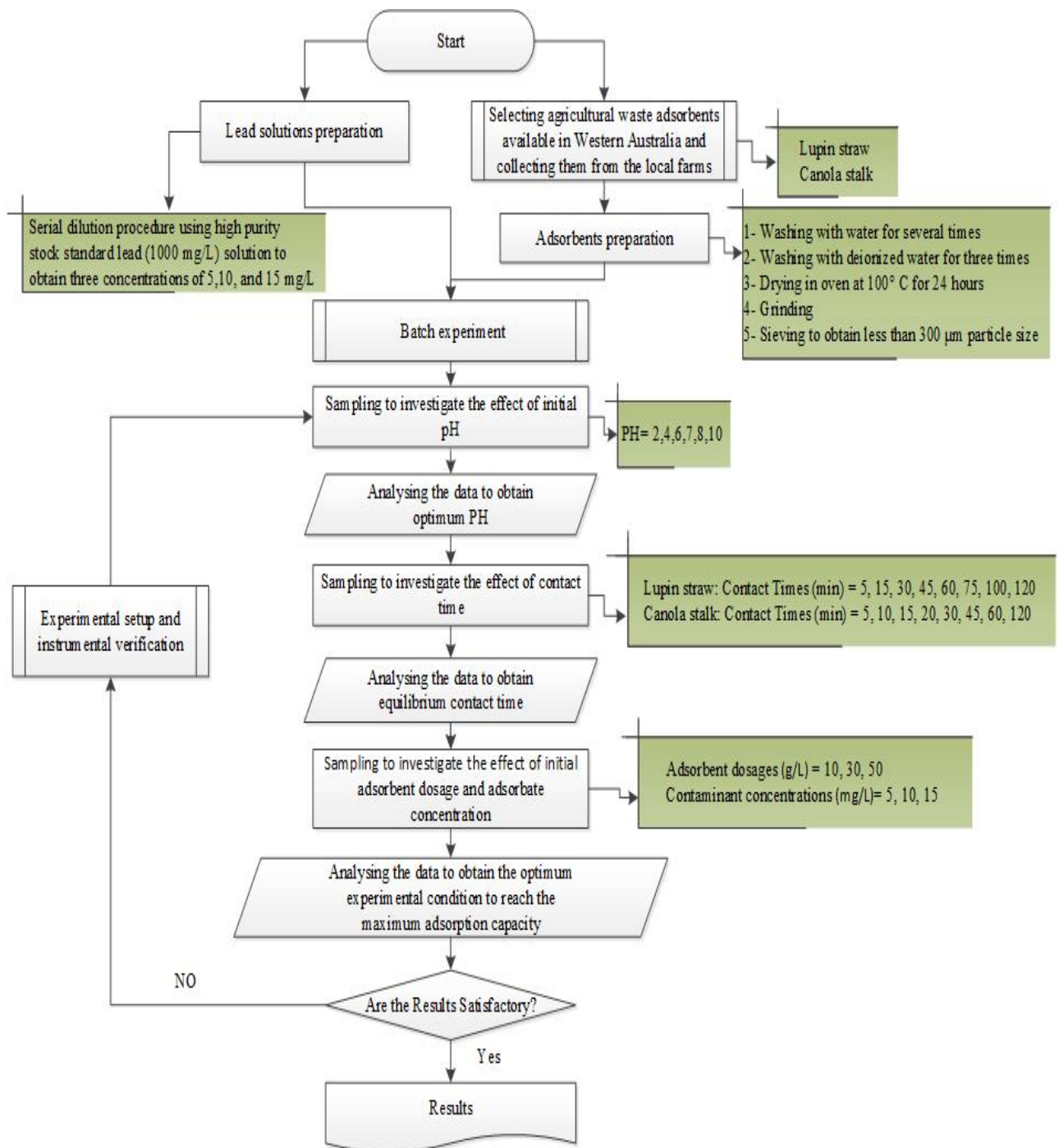
Figure 4. Experimental sampling process schematic for each adsorbent

3.8 Data collection and analysis

After completing the sampling procedure and filtering the solutions, microwave plasma atomic emission spectroscopy (MP-AES) was used to measure the residual concentrations of Pb (II) ions after the experiment. The adsorbents residues also were analysed to investigate their surface morphology and characterization. For this purpose, the research project used the scanning electron microscopy (SEM) system. This is a reliable technique capable of imaging the surface of the materials to study their morphology and roughness before and after the experiment. The spatial properties of adsorbent surfaces

have a significant influence on the initial stages of adsorption process. Energy- dispersive X-ray spectroscopy (EDX) was employed as an analytical technique to analyse the elements or chemical characterization of the adsorbents based on the interaction between X-ray beams and the surface of the material. The identification of the functional and anionic groups which are responsible for the adsorption process on the surface of the adsorbents was investigated using Fourier transform infrared (FTIR) spectral analysis before and after the experiment.

3.8.1   Data analysis schematic

Figure 5 shows the schematic flowchart of the data analysing procedure and identifying the surface characteristics of the adsorbents. This procedure was followed to analyse the experimental data relating to lead elimination from aqueous solutions using lupin straw and canola stalk.
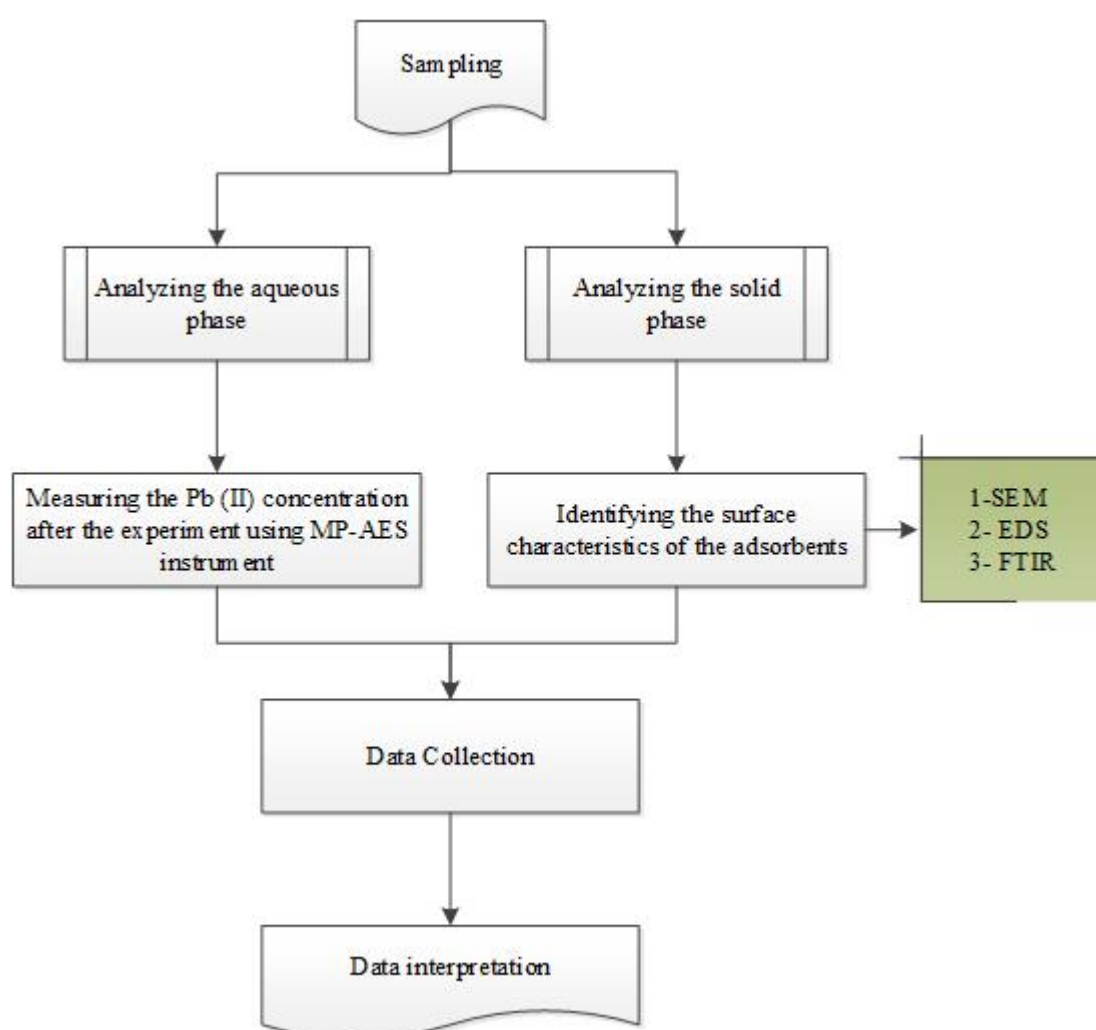
Figure 5. Data analysing procedure and identifying the surface characteristics of the adsorbents.

3.9   Conclusion

This chapter has provided the methodology of getting the experimental data. In addition, all the experimental data and surface characteristics analysis of both adsorbents before and after the

experimentation were collected at this stage to investigate the efficiency of the adsorbents in regards to the removal of Pb (II) from aqueous solutions at low concentrations. The data were evaluated with different isotherm and kinetic modellings to study the adsorption process. Chapter 5 and Chapter 6 will present the result and discussions of these findings. Next chapter will explain the theory behind the different isotherm and kinetic models used and describe how all the parameters of isotherm and kinetic equations were calculated. Chapter 4 also explains how experimental data was evaluated using these equations to understand the adsorption process based on the theory and assumption behind used isotherm and kinetic models.

Chapter-4

4 Theory of the isotherm and kinetic models

4.1 Introduction

Modelling of the obtained experimental data helps to predict and understand the effectiveness of the adsorption mechanism of different adsorption systems. Isotherm studies describe the homogeneity of the surface of the adsorbents. In this research the Langmuir, Freundlich, Harkins-Jura, Redlich-Peterson and Halsey isotherm models were used to investigate sorption equilibrium for lead removal from aqueous solutions using lupin straw and canola stalk. Linear and non-linear forms of all isotherm equations are presented in the section below.

The physical and chemical properties of the adsorbent influence the adsorption process. Thus, this research has proposed different kinetic models to evaluate reaction pathways over time and investigate whether the process is based on physisorption or chemisorption interactions based on mass transfer resistance. In this study, five different kinetic models were applied to investigate the adsorption process under different experimental parameters such as adsorbate concentration and contact time. The sections below will look at each of the five isotherm and kinetic models in turn.

4.2 Isotherm models

4.2.1 Langmuir isotherm model

The Langmuir is a two-parameter isotherm model which was developed based on the assumption that all of the active sites for the adsorption process have an equal affinity for binding. This isotherm model describes the surface of the adsorbent as homogeneous (Langmuir, 1916). The Langmuir non-linear equation is as follows:

$$q_e = \frac{b_l C_e q_l}{1 + b_l C_e} \tag{3}$$

Where, q_e = the experimental equilibrium adsorption capacity (mg/g); C_e= equilibrium adsorbate concentration (mg/L); b_l , q_l = Langmuir constants;

After considering the initial and final boundary conditions, the non-linear equation changes to the linear form equation as:

$$\frac{C_e}{q_e} = \frac{C_e}{q_l} + \frac{1}{b_l q_l} \tag{4}$$

In the Langmuir isotherm, the constant values of b_l and q_l (the equilibrium capacity) can be obtained from the intercept and slope of the plot $\frac{C_e}{q_l}$ versus C_e respectively.

4.2.2 Freundlich isotherm model

The Freunlich isotherm is a two-parameter model which is able to accurately describe the process of adsorption onto a heterogeneous adsorbent surface. In this isotherm, stronger binding sites are usually occupied at the beginning of the adsorption process and the affinity for binding then decreases over time (Freundlich, 1907). The non-linear form of the Freundlich equation is:

$$q_e = K_f C_e^{\frac{1}{n_f}} \tag{5}$$

Where, the K_f and n_f are the Freundlich constant parameters. The linear form of this equation can be presented as follows:

$$\log(q_e) = \log(K_f) + \frac{1}{n_f} \log(C_e) \tag{6}$$

In the Freundlich isotherm the constant values of n_f and K_f can be calculated from the intercept and slope of the plot $\log(q_e)$ vs $\log(C_e)$ respectively.

4.2.3 Harkins-Jura isotherm model

The possibility of a multilayer adsorption process assumed in the Harkins-Jura isotherm can be explained by the presence of heterogeneous pore distribution and heteroporous solids, respectively (Amin, 2009; Başar, 2006). The non-linear equation of this two-parameter isotherm is shown as follows (Harkins and Jura, 1944):

$$q_e = \left(\frac{A_H}{B_H - \log C_e}\right)^{\frac{1}{2}} \tag{7}$$

Where, the A_H and B_H are the constant parameters of the Harkins-Jura isotherm. The linear form of this equation is:

$$\frac{1}{q_e^2} = \left(\frac{B_H}{A_H}\right) - \left(\frac{1}{A_H}\right) \log C_e \tag{8}$$

The constant parameters (A_H and B_H) of the Harkins-Jura equation can be determined from the plot $\frac{1}{q_e^2}$ versus $\log C_e$.

4.2.4 Redlich-Peterson isotherm model

The Redlich-Peterson isotherm is a combination of the Langmuir and Freundlich isotherms incorporating three elements. Consequently, this isotherm is applicable to either heterogeneous or homogeneous surfaces of the adsorbent. The mixed adsorption process in the Redlich-Peterson isotherm

does not follow ideal monolayer adsorption. The non-linear equation of this isotherm is expressed as (Jossens et al., 1978):

$$q_e = \frac{A_R C_e}{1 + B_R C_e^\beta} \tag{9}$$

Where, A_R, B_R, and β are Redlich-Peterson constant parameters. The linear form of this equation is presented as:

$$\ln\left(A_R \frac{C_e}{q_e} - 1\right) = \beta \ln C_e + \ln B_R \tag{10}$$

The Redlich-Peterson constant parameters A_R, B_R, and β can be obtained from the intercept and slope of plotting $\ln\left(A_R \frac{C_e}{q_e} - 1\right)$ versus $\ln C_e$, respectively.

4.2.5 Halsey isotherm model

The Halsey isotherm is a two-parameter model which usually evaluates non-uniform surfaces and multilayer adsorption processes. The non-linear equation of the Halsey isotherm can be expressed as follows (Halsey, 1948):

$$q_e = \left(\frac{k_H}{\ln(C_e)}\right)^{\frac{1}{n_H}} \tag{11}$$

Where, k_H and n_H are Hasley constant parameters. The linear form of this equation is presented as:

$$\ln q_e = \left[\left(\frac{1}{n_H}\right)\ln k_H\right] - \left(\frac{1}{n_H}\right)\ln C_e \tag{12}$$

The constant parameters of the Halsey isotherm (k_H and n_H) can be determined from the slope and intercept of the plot of $\ln q_e$ versus $\ln C_e$, respectively.

4.3 Kinetic models

4.3.1 Pseudo-first-order kinetic model

The pseudo-first order equation (Lagergren, 1898) has been proposed to describe the adsorption reaction for the liquid-solid adsorption systems. The non-linear form of this model is represented by the following equation:

$$\frac{dq_t}{dt} = K_f(q_e - q_t) \tag{13}$$

While after considering initial and final boundary conditions (t=0 – t and q_t= 0- q_t), the pseudo-first-order model changes to the following linear equation (Aharoni and Sparks, 1991):

$$\log(q_e - q_t) = \log(q_e) - \frac{K_f}{2.303}t \qquad (14)$$

Where, q_t is the amount of lead adsorbed by lupin straw at time "t" and K_f is a constant value that can be calculated from the slop of the plot $\log(q_e - q_t)$ versus time.

4.3.2 Pseudo-second-order kinetic model

This kinetic model was developed based on the chemisorption interaction between the adsorbate and the surface of the adsorbent that involving wan-der-Waals forces through the exchange of electrons. The non-linear form of this model is expressed as below:

$$\frac{dq}{dt} = K_S(q_e - q_t)^2 \qquad Q$$

While after considering the boundary conditions (t=0 – t and q_t= 0- q_t), the linear form can be obtained as follows (Ho and McKay, 1999):

$$\frac{t}{q_t} = \frac{1}{K_s q_e^2} + \frac{1}{q_e}t \qquad (15)$$

Where, K_s is the constant value of equilibrium rate and can be obtained from the plot $\frac{t}{q_t}$ versus t.

4.3.3 Intra-particle diffusion kinetic model

The intraparticle diffusion kinetic model has been widely used in order to investigate the mechanism of adsorption (Al Duri and Mckay, 1990). Several factors affect the adsorption mechanism of this kinetic model, including equilibrium behaviour, chemical and physical structures of the adsorbent, and experimental conditions. In this kinetic model, the solute adsorbate particles diffuse to the adsorbate sites through the liquid phase. This diffusion can be a combination of surface diffusion and pore-volume diffusion. Weber and Morris suggested an equation for this kinetic model as follows (Rauf et al., 1996):

$$q_t = K_i t^{\frac{1}{2}} + C_i \qquad (16)$$

Where K_i (mg/gmin$^{\frac{1}{2}}$) is the intraparticle diffusion rate constant and C_i (mg/g) is a constant value of the equation. The intercept value has a direct relationship with the boundary layer effect (Wu et al., 2009). The constant parameters can be obtained using the intercept and slop of the plot q_t against the square root of time ($t^{\frac{1}{2}}$).

4.3.4 Elovich kinetic model

The Elovich kinetic model describes the chemical adsorption interaction between the adsorbate and adsorbent. The non-linear equation form of the Elovich kinetic model can be represented as follows (Low, 1960)

$$q_t = \frac{1}{\beta}\ln(1 + \alpha\beta t) \tag{17}$$

After considering the boundary conditions (t=0 – t and q_t= 0- q_t) assuming that $\alpha\beta t \gg 1$, the linear form of the equation is obtained as below (Chien and Clayton, 1980):

$$q_t = \beta\ln(t) + \alpha \tag{18}$$

Where, α is the constant initial lead adsorption rate and β is the adsorption constant. The constant values can be calculated from the intercept and slop of the plot q_t versus $\ln(t)$.

4.3.5 Fractional power kinetic model

The fractional power kinetic model could be expressed by following equation (Dalal, 1974):

$$q_t = \varepsilon t^\omega \tag{19}$$

The linear form can be calculated as bellow:

$$\ln(q_t) = \ln(\varepsilon) + \omega\ln(t) \tag{20}$$

Where, ε is a constant value of adsorption rate at unit time and ω is a constant value<1. The constant values can be calculated from the intercept and slop of the plot $\ln(q_t)$ versus $\ln(t)$.

4.4 Conclusion

Isotherm studies describe the surface of the adsorbent as homogeneous (Langmuir isotherm) and heterogeneous (Freundlich, Harkins-Jura, and Halsey isotherms). The kinetic studies describe the adsorption process as chemisorption, physisorption, or a combination of both. After considering initial and final boundary conditions (t=0 – t and q_t= 0- q_t), the non-linear equations become linear and the constant parameters of the described models can be obtained from the slop and intercept of the linear form plots. The isotherm and kinetic models fit the experimental data well due to the high correlation of coefficient values.

This chapter reviewed the theory and equations relating to the utilized isotherm and kinetic studies in this thesis. Chapter 5 and Chapter 6 will present the obtained experimental and modelling results of using lupin straw and canola stalk as adsorbents for the removal of lead ions from wastewater and will discuss about all the findings of this research.

Chapter 5

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Chapter-7

7 Conclusions and recommendations for future work

7.1 Conclusions

The study presented in this thesis highlights the fact that lupin straw and canola stalk are highly effective, economical, biodegradable, and environmentally clean adsorbents that can be used to remove Pb (II) from contaminated water. The main advantage of using raw agricultural waste materials as adsorbents is the ability to minimize the amount of chemicals added to the water during the water purification process. Chemical and thermal pre-treatment of agro-wastes mostly involve expensive and energy-intensive processes. More importantly, chemically pre-treated agro-waste may release some unwanted by-products into water, creating a need for further treatment procedures.

In this study, lupin straw successfully removed 98.4% of Pb (II) ions, and canola stalk successfully removed 98%. Table 8 shows the percentage removal of lead as reported in this study, and the percentages reported for other agricultural waste adsorbents in previous studies.

Although lupin straw removed a higher percentage of Pb (II) ions than canola stalk, the adsorption capacity of canola stalk was higher. The maximum adsorption capacities vary based on the surface characteristics, chemical composition, and functional groups of each adsorbent. In addition, the experimental and operational conditions influence the sorption capacities. Table 14 demonstrates the maximum adsorption capacities of lead ions onto various agricultural waste adsorbents.

Comparing the results of using lupin straw and canola stalk for the sequestration of lead in low concentrations indicates the differences between these two adsorbents. The optimum pH for lupin straw it was found at pH=5.5, while for canola straw was obtained at pH=4. The equilibrium time for canola stalk was reached after 30 minutes, whereas the active sites on the surface of the lupin straw were saturated after 60 minutes. The adsorbent dosage for both agricultural waste adsorbents was 10 g/L, and the lead concentration for both experiments was 5 mg/L. Both adsorbents followed the Freundlich and Halsey isotherm models. The pseudo-second-order kinetic equation best described the adsorption mechanism of lead ions onto both adsorbents, followed by intra-particle diffusion. The FTIR studies of the surface of both adsorbents revealed the existence of cellulose and lignin due to the presence of different kinds of hydroxyl, carboxyl, and phenol groups on their surfaces. According to the obtained high percentage removal of Pb (II) ions by lupin straw and canola stalk and comparable adsorption capacities of them with other bio-sorbents, it can be concluded that lupin straw and canola stalk are adsorbents that are highly effective at removing lead from aqueous solutions.

7.2 Future work recommendation

Although extensive studies have been carried out on the adsorption process, more work is needed in relation to the performance and cost of the process. Due to the fact that all of the experiments have

been done on a laboratory scale, the effectiveness of the adsorption process in an industrial scale need to be investigated.

In this study, lupin straw and canola stalk were used to eliminate Pb (II) as a toxic heavy metal from aqueous solutions. These adsorbents can be also used to remove other contaminants such as dyes, organic materials, proteins, peptides, and antibodies. Additional studies are also needed to evaluate the ability of lupin straw to remove other heavy metals from wastewater. In this regard, some studies such as desorption, mixed adsorbents, mixed adsorbates, and column study need to be investigated.

Utilizing a hybrid purification mechanism by combining some purification processes can also enhance the performance of the water treatment process, especially on a large industrial scale. For instance, combining photochemical with bio-sorption processes may improve the contaminant removal efficiency. In this regard, it may be possible to apply modifications to facilitate ion exchange process and develop the active sites on the adsorbent surface. However, the cost of the modifications and final disposal of the adsorbents need to be considered in relation to economic profitability and performance effectiveness in the context of functioning industrial-scale wastewater treatment plants.

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Appendix I

This appendix provides information about the dispersion of crop and cereal straws in Western Australia. This information is reported by Department of Agriculture and Food, Western Australia (DAFWA).

Table 16. Dispersion of cereal residues and crop straws in Western Australia
(http://nationalmap.gov.au/renewables)

Production level	Local government areas _name_2015	Straw yield /ha cereal crop Average over 5 years	Average shire yield of cereal residue (tonnes)
2.5 - 3	Albany (C)	2.53	46237.87333
2 - 2.5	Beverley (S)	2.14	84721.80178
2.5 - 3	Boddington (S)	2.62	8652.844578
2.5 - 3	Boyup Brook (S)	2.65	20485.96889
1 - 1.5	Brookton (S)	1.47	54339.41776
2 - 2.5	Broomehill-Tambellup (S)	2.12	146358.239
1 - 1.5	Bruce Rock (S)	1.04	124427.3857
0.5 - 1	Carnamah (S)	0.85	47604.60984
1.5 - 2	Chapman Valley (S)	1.58	163887.6556
2 - 2.5	Chittering (S)	2.39	14005.33
0.5 - 1	Coorow (S)	0.74	44921
0.5 - 1	Corrigin (S)	0.93	90820.1448
2 - 2.5	Cranbrook (S)	2.21	47503.04
1.5 - 2	Cuballing (S)	1.66	35857.84267
1 - 1.5	Cunderdin (S)	1.46	113235.206
1 - 1.5	Dalwallinu (S)	1.32	304864.92
2.5 - 3	Dandaragan (S)	2.98	70509.10222
1 - 1.5	Dowerin (S)	1.22	90543.78444
1.5 - 2	Dumbleyung (S)	1.6	129134.3978
2 - 2.5	Esperance (S)	2.48	996889.16
1.5 - 2	Geraldton-Greenough (S)	1.6	53071.31333
2 - 2.5	Gingin (S)	2.28	2341.191333

1.5 - 2	Gnowangerup (S)	1.92	209393.6133
1.5 - 2	Goomalling (S)	1.86	114245.0128
1.5 - 2	Irwin (S)	1.98	28675.30889
1.5 - 2	Jerramungup (S)	1.84	153570.9756
1.5 - 2	Katanning (S)	1.91	73582.69333
1 - 1.5	Kellerberrin (S)	1.23	82085.87619
1 - 1.5	Kent (S)	1.46	191401.98
2 - 2.5	Kojonup (S)	2.33	60823.21556
1 - 1.5	Kondinin (S)	1.09	162419.2667
0.5 - 1	Koorda (S)	0.58	36053.30805
0.5 - 1	Kulin (S)	0.97	142893.0111
1 - 1.5	Lake Grace (S)	1.12	371190.9778
0.5 - 1	Merredin (S)	0.77	86992.93029
1.5 - 2	Mingenew (S)	1.73	117814.4533
2 - 2.5	Moora (S)	2.18	211339.7233
0.5 - 1	Morawa (S)	0.57	41553.84
0.5 - 1	Mount Marshall (S)	0.69	80921.45116
0.5 - 1	Mukinbudin (S)	0.72	74012.1534
0.5 - 1	Mullewa (S)	0.89	107611.0889
0.5 - 1	Narembeen (S)	0.9	111332.9648
1.5 - 2	Narrogin (S)	1.78	57519.31604
2 - 2.5	Northam (S)	2.13	46511.97302
1 - 1.5	Northampton (S)	1.34	125626.2422
0.5 - 1	Nungarin (S)	0.67	32196.87069
0 - 0.5	Perenjori (S)	0	0
1 - 1.5	Pingelly (S)	1.5	46812.51907
2.5 - 3	Plantagenet (S)	2.53	52712.63333
1.5 - 2	Quairading (S)	1.57	106119.014
1.5 - 2	Ravensthorpe (S)	1.76	213718.4933
0.5 - 1	Tammin (S)	0.97	45927.90689
0.5 - 1	Three Springs (S)	1	55858.60645

2 - 2.5	Toodyay (S)	2.24	34152.65462
0.5 - 1	Trayning (S)	0.72	37616.04805
2 - 2.5	Victoria Plains (S)	2.42	143041.0867
1.5 - 2	Wagin (S)	1.68	78891.97667
2 - 2.5	Wandering (S)	2.05	26998.56184
2 - 2.5	West Arthur (S)	2.33	50230.06667
0.5 - 1	Westonia (S)	0.7	72097.44844
1 - 1.5	Wickepin (S)	1.13	64730.71716
2 - 2.5	Williams (S)	2.14	48779.466
1.5 - 2	Wongan-Ballidu (S)	1.74	203734.8744
2 - 2.5	Woodanilling (S)	2.15	37770.35778
0.5 - 1	Wyalkatchem (S)	0.74	43755.31311
0 - 0.5	Yilgarn (S)	0.5	84152.48979
2 - 2.5	York (S)	2.11	72406.10489

At the author's request,

Appendix II is not available in this version of the thesis.